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Research Contract N00014-87-K-0014

R&T Code 413E026---01

Technical Report No. 12

CHEMICAL COMPATIBILITY OF HIGH-T_c SUPERCONDUCTORS WITH OTHER MATERIALS

by

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In Press

in

"Physical Chemistry of High-Temperature Superconductors"
D.L. Nelson and T.F. George, eds.
American Chemical Society

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July, 1988

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UNCLASSIFIED
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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS N/A
2a SECURITY CLASSIFICATION AUTHORITY N/A	3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b DECLASSIFICATION / DOWNGRADING SCHEDULE N/A	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION The Regents of the University of California 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION 1) ONR Pasadena - Administrative 2) ONR Alexandria - Technical
6c ADDRESS (City, State, and ZIP Code) Office of Contracts & Grants Administration U C L A, 405 Hilgard Avenue Los Angeles, CA 90024	7b ADDRESS (City, State, and ZIP Code) 1) 1030 E. Green Street, Pasadena, CA 91106 2) 800 N. Quincy St., Arlington, VA 22217-5000
8a NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b OFFICE SYMBOL (If applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0014
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street, 614A:DHP Arlington, VA 22217-5000	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
UNCLASSIFIED: Tech Rept#12 CHEMICAL COMPATIBILITY OF HIGH-T_c SUPERCONDUCTORS WITH OTHER MATERIALS

12 PERSONAL AUTHOR(S) R.S. Williams and S. Chaudhury

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical Preprint	FROM Aug '87 TO July '88	1988: July 22	5 + Figs

16 SUPPLEMENTARY NOTATION

17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	oxide superconductors, sintering and annealing at high-T - 1-2-3 phases - chemical stability.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In any application, the new oxide superconductors will have to coexist in intimate contact with other materials. However, the copper-oxygen bonds common to all presently known oxide superconductors with T_c above 40K are relatively weak. This means that elements that form much stronger bonds with oxygen, such as Si, will be chemically unstable when in contact with the copper-oxide superconductors. In this paper, we will establish procedures and guidelines that will enable workers to choose materials that will not react chemically with the oxide superconductors. These should enable researchers working in all applications areas to avoid unnecessary empirical searches for suitable substrate or host materials by eliminating the most thermodynamically unfavorable choices. In particular, we have determined which of the elemental metals should be most stable in contact with the copper-oxide semiconductors, and examined schemes for integrating these superconductors into Si devices.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL R. Stanley Williams	22b TELEPHONE (Include Area Code) (213) 825-8818 22c OFFICE SYMBOL UCLA

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

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Chemical Compatibility of High-T_c Superconductors with Other Materials

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In any application, the new oxide superconductors will have to coexist in intimate contact with other materials. However, the copper-oxygen bonds common to all presently known oxide superconductors with T_c above 40K are relatively weak. This means that elements that form much stronger bonds with oxygen, such as Si, will be chemically unstable when in contact with the copper-oxide superconductors. In this paper, we will establish procedures and guidelines that will enable workers to choose materials that will not react chemically with the oxide super-conductors. These should enable researchers working in all applications areas to avoid unnecessary empirical searches for suitable substrate or host materials by eliminating the most thermo-dynamically unfavorable choices. In particular, we have determined which of the elemental metals should be most stable in contact with the copper-oxide semi-conductors, and examined schemes for integrating these superconductors into Si devices.

Introduction

There has been a great deal of research over the past year on the new oxide superconductors. Justifiably, most of that work has concentrated on the preparation of materials with optimized properties; i.e., maximized T_c and critical currents. This is the proper time to think in broad terms about how to successfully encorporate the new superconductors into structures that will serve useful purposes. Particular attention must be paid to the processing of these structures, especially if any of the steps involve sintering or annealing steps at reasonably high temperatures (i.e., 700K or above).

The superconducting 1-2-3 phases are known to be chemically sensitive, and in fact are thought to be metastable compounds under all conditions of temperature and oxygen partial pressure (1). Thus, it is imperative that any material in intimate contact with 1-2-3 phases does not react with the component oxides to form more stable compounds, since such a reaction will destroy the superconducting material. This is especially important for thin film applications, since the amount of superconductor is small compared to that of the substrate, and the diffusion path for potential solid state reactions, i.e., the film thickness, is very short. In this paper we will concentrate on searching for materials that should be most stable in contact with the 1-2-3 superconductors, since they appear to be more sensitive to chemical disruption than the more recently discovered Bi- and Tl-based phases. The principles and much of the data presented here can be applied to any oxide superconductor, whether it is presently known or yet to be discovered.

The reason for the chemical vulnerability of phases based on copper oxides is shown in Fig. 1, which is a display of the heat of formation per gram-atom of the most stable solid oxides formed by the metallic and semiconducting elements in the periodic table. To generate this table, compilations of thermochemical data were consulted (2,3), and these sources provided the enthalpies of formation used for the calculations presented later. The reason for expressing the data in the manner shown in Fig.1 is to get an idea of the relative strengths of the M-O bonds that form the solid oxides. One can see immediately that very few elements form weaker bonds with O than does Cu. Thus, most elements will reduce CuO to elemental Cu, and are very likely to react chemically with any of the copper-oxide superconductors as well. Although a positive heat of reaction, determined for interactions of the 1-2-3 superconductors with another material, is not a sufficient condition for chemical stability, it is almost certainly necessary. Consequently, researchers interested in the processing of copper-oxide superconductors into structures should consider thermochemical properties carefully.

In this investigation, we have collected the relevant heats of formation and phase diagrams to analyze the stability of 1-2-3 compounds with respect to the solid elements and several oxides. To check that the thermochemical predictions are indeed correct, we have made use of reports of chemical reactivity in the literature, and have also performed simple experiments to determine whether or not 1-2-3 will react with another material and identify the reaction products when it does. The next section describes the experimental procedure followed in this study; the results and conclusions to be drawn from this paper are presented in the succeeding sections.

Experimental Procedure

The reactivities of various materials with respect to $YBa_2Cu_3O_{7-x}$ were determined by heating mixtures of carefully weighed powders sealed in quartz ampoules. The 1-2-3 material, prepared by the citrate precipitation process (4), was obtained from the research group of Prof. Richard Kaner at UCLA. The other materials were reagent grade chemicals obtained from our stockroom. Small amounts of the mixed powders were reserved for x-ray powder diffraction analysis so that the phases present before and after heating could be compared. The ampoules were placed in a furnace at 1073K for four hours to initiate any reactions. The intent here was not to determine the

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equilibrium products of the multi-element systems, but just to see if indeed a reaction did occur. Both heated and unheated mixtures, as well as control samples that were single compounds sealed in ampoules and heated, were examined by x-ray powder diffractometry. The diffractometer was computer controlled, and data collection times as long as 12 hours were used to obtain a reasonable signal-to-noise ratio. These studies showed that the 1-2-3 material by itself did not react with the quartz tubes during the heating cycle, but mixtures of 1-2-3 with other materials often did attack the quartz.

Chemical Stability of 1-2-3 with Respect to Elements

There are only nine elemental metals that will not reduce CuO: Ru, Rh, Pd, Ag, Os, Ir, Pt, Au, and Hg. These are grouped with a bold border in the periodic table of Fig. 1. No solid oxide of Au is stable, and the oxides of Pd, Ag, Pt, and Hg are just barely stable. The chemical formula of the oxides of Ru, Os, and Ir is MO_2, so two equivalents of CuO would be required to oxidize one equivalent of these metals by the reaction $M + 2CuO \rightarrow MO_2 + 2Cu$. For Rh, the oxide is Rh_2O_3, so three equivalents of CuO would be required to produce one equivalent of Rh_2O_3. Thus, CuO is also stable with respect to these last four metals because the heat of formation of two (or three) equivalents of CuO is larger in magnitude than a single equivalent of the oxides of Ru, Os, and Ir (or Rh). Therefore, these nine metals are the only elements that may not react chemically with 1-2-3 superconductors, although each individual system should be checked to ensure that they are indeed stable.

We can actually use the reactivity or lack thereof of the 1-2-3 com-pounds with different elements to determine roughly the heat of formation of the superconductor. For the purposes of this paper, we will assume that 1-2-3 is a stable compound and that it has the ideal formula $YBa_2Cu_3O_{6.5}$. Thus, the reaction

$$1/2Y_2O_3 + 2BaO + 3CuO \rightarrow YBa_2Cu_3O_{6.5} \qquad (1)$$

has an unknown but negative heat of reaction, ΔH_f, or the heat of formation with respect to the component oxides. We can place a lower limit on this value by considering a reaction between the 1-2-3 material and an element that is just barely above the threshold for reaction with CuO. The most suitable element for this purpose is Tl, since

$$2Tl + CuO \rightarrow Tl_2O + Cu \;; \qquad \Delta H_1 = -2.9(\pm 2.6)\text{ kcal.} \qquad (2)$$

However, because of our lack of facilities to handle toxic materials, we chose instead to try the next best choice, which is Pb:

$$Pb + CuO \rightarrow PbO + Cu \;; \quad \Delta H_2 = -15.3\ (\pm 1.0)\text{ kcal.} \qquad (3)$$

If we consider the idealized reaction between Pb and 1-2-3,

$$3Pb + YBa_2Cu_3O_{6.5} \rightarrow 1/2Y_2O_3 + 2BaO + 3PbO + 3Cu \;; \quad \Delta H_3 = ?, \qquad (4)$$

and this reaction is exothermic, then we can obtain limits for ΔH_f as follows:

$$0 > \Delta H_f = 3\Delta H_2 - \Delta H_3 > 3\Delta H_2 = -46\text{ kcal,} \qquad (5)$$

where the second inequality holds because minus ΔH_3 is a positive number. We have carried out the reaction indicated by Eq.(4), and we do observe the appearance of elemental Cu in the reaction products. Although the uncertainty in the estimate that we obtain appears to be large, the limits that

we place on ΔH_f do allow us to make some quantitative predictions with respect to the reactions of 1-2-3 with other elements and compounds. If we predict that 1-2-3 will react based on the above lower limit for ΔH_f, we can be very confident in our prediction since ΔH_f may even be slightly positive (1).

Chemical Stability of 1-2-3 with Respect to Si and Insulators

For many applications, a noble or near-noble metal cladding for copper-oxide superconductors may be perfectly acceptable. However, one of the primary uses envisioned for high-T_c superconductors is as a conductor on semiconductor devices. It is obvious that 1-2-3 will not be stable as a thin film on a bare Si substrate, since

$$Si + 2CuO \longrightarrow SiO_2 + 2Cu \quad ; \quad \Delta H_4 = -143 \text{ kcal} \ . \qquad (6)$$

Thus, one may predict

$$3/2Si + YBa_2Cu_3O_{6.5} \longrightarrow 1/2Y_2O_3 + 2BaO + 3/2SiO_2 + 3Cu \qquad (7)$$

where

$$-97 \text{ kcal} > \Delta H_5 > -143 \text{ kcal}. \qquad (8)$$

In fact, mixing Si and 1-2-3 in the proportions shown in Eq.(7) and heating immediately yields a brown powder, which contains elemental Cu and various silicates.

An obvious idea is to use a layer of inert insulating material between the Si and the superconductor, such as SiO_2. However, here we run into the problem of silicate formation via the following reaction:

$$SiO_2 + 2BaO \longrightarrow Ba_2SiO_4 \quad ; \quad \Delta H_6 = -64.5 \text{ kcal}, \qquad (9)$$

which is more exothermic than the estimate of Eq.(5) for the heat of formation of 1-2-3 from its component oxides. A stabilizing layer of aluminum oxide does not appear to be much more useful, since

$$2Al_2O_3 + 2BaO \longrightarrow 2BaAl_2O_4 \quad ; \quad \Delta H_7 = -48.0 \text{ kcal}, \qquad (10)$$

which means that 1-2-3 probably reacts with Al_2O_3 as well. Thus, any processing procedure that will require a high temperature annealing of the superconductor after it has been deposited onto the Si wafer will require careful thought to design a suitable buffer layer.

Another possibility that comes to mind is to use Y_2O_3. However, this is also not a reasonable choice. Examination of the quasi-ternary phase diagram in Fig.2 that has been generated for the CuO-BaO-$YO_{1.5}$ system (5) reveals that there is no tie-line connecting 1-2-3 with Y_2O_3. This means that these two compounds will react with each other to produce the 2-1-1 compound and either CuO or $Y_2Cu_2O_5$, depending on the relative amounts of the starting materials. The three compounds that do form tie-lines to 1-2-3 are 2-1-1, CuO, and $BaCuO_2$. Neither CuO nor $BaCuO_2$ could be effective barriers, since both contain fragile Cu-O bonds that will be the focus of any chemical attack by other materials.

One might consider growing a multilayer insulating film with the structure SiO_2/Y_2O_3/2-1-1/1-2-3. This may also lead to problems, since the SiO_2 and the Y_2O_3 can react to form two different silicates, Y_2SiO_5 and $Y_2Si_2O_7$. Thus, a barrier layer involving Y_2O_3 would involve as many as five different films to separate 1-2-3 from Si and ensure that the materials in contact at each interface are chemically stable with respect to each other. Such complex structures should be avoided, since they will be difficult and expensive to produce.

Probably the best strategy is to search for a compound that is stable with respect to both 1-2-3 and to SiO_2. In principle, this requires that the phase diagram in Fig. 2 be generalized to a pseudo-quaternary diagram by including all the interactions of SiO_2 with the other phases. At present, only the compounds on the edges of the resulting tetrahedron that share the SiO_2 apex are known, and they are shown on the three pseudo-ternary diagrams in Figs. 3-5.

It is possible to make a good guess at the topology of both the pseudo-ternary phase diagrams in the SiO_2-Y_2O_3-CuO (Fig.3) and the SiO_2-BaO-CuO (Fig.4) systems. Since there are no copper silicates, it is unlikely that there are any pseudo-ternary compounds in either phase diagram. Moreover, the yttrium and barium silicates are very stable, so SiO_2 is likely to replace CuO in compounds with BaO or Y_2O_3. With these assumptions, the tie-lines in Figs.3 and 4 are the most logical ways of connecting the pseudo-binary compounds across the phase diagrams. The SiO_2-Y_2O_3-BaO system outlined in Fig.5, however, is much too complex to allow a phase diagram to be determined by guesswork. There are almost certainly pseudo-ternary compounds in this system, and there are no thermo-chemical data for the pseudo-binary compounds on the boundaries of the phase diagram. Thus, this system will have to be investigated in detail experimentally.

It would be fortunate if there were a tie-line cutting through the pseudo-quaternary system to connect 1-2-3 with either $Y_2Si_2O_7$ or $BaSi_2O_5$. The former is not very likely, since the CuO-211-BaY_2O_4 tie-lines shown in Fig.2 are probably part of a plane that effectively isolates 1-2-3 from Y_2O_3-rich species in the pseudo-quaternary system. The latter case was a possibility that we investigated. No reaction was observed between powders of 1-2-3 and $BaSi_2O_5$ heated to 973 K for 24 hours, which means that these materials do terminate a tie line. The *caveat* is that the silicate is apparently suitable as a buffer layer in terms of thermodynamic properties, but it may have other undesirable qualities, such as poor mechanical properties, rough film morphology, or severe lattice mismatch. These properties are the subject of further research.

Chemical Stability of 1-2-3 in Air

The 1-2-3 compounds are notoriously unstable with respect to CO_2 and H_2O in the air. This is the result of the large enthalpies of formation of $BaCO_3$ and $Ba(OH)_2$ from the following reactions:

$$BaO + H_2O \longrightarrow Ba(OH)_2 \; ; \; \Delta H_8 = -35.4 \text{ kcal} \qquad (11)$$

and

$$BaO + CO_2 \longrightarrow BaCO_3 \; ; \; \Delta H_9 = -64.4 \text{ kcal} . \qquad (12)$$

Thus, we see that the reactivity of BaO with other oxides is a major factor in the chemical sensitivity of 1-2-3. The high-T_c superconductors that do not contain BaO should be significantly more stable than 1-2-3, and most likely much easier to process in the presence of other materials.

Acknowledgments

We thank B. Dunn and R.B. Kaner for their advice and help. This work was supported in part by the Office of Naval Research.

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Figure Captions:

Figure 1. Periodic table of the elements showing the heat of formation (in kcal/gram-atom) of the most stable solid oxide of each element. The more negative the value of ΔH_f, the more strongly the element bonds to oxygen. (Data were taken from Refs. 2 and 3.)

Figure 2. Idealized pseudo-ternary phase diagram for the Y_2O_3-BaO-CuO system, showing only the solid phases. (Adapted from Ref. 5.)

Figure 3. Idealized pseudo-ternary phase diagram for the SiO_2-Y_2O_3-CuO system, showing only the solid phases. The tie-lines were drawn based on the assumption that no pseudo-ternary compounds form.

Figure 4. Idealized pseudo-ternary phase diagram for the SiO_2-CuO-BaO system, showing only the solid phases. The tie-lines were drawn based on the assumption that no pseudo-ternary compounds form.

Figure 5. The boundary of the pseudo-ternary phase diagram for the SiO_2-BaO-Y_2O_3 system. Since it is almost certain that pseudo-ternary compounds exist in this system, no attempt has been made to estimate the positions of the tie-lines.

Periodic Table of the Elements

ΔH_f (heat of formation) in kcal/gm atom
for stable solid oxides

IA	IIA	IIIA	IVA	VA	VIA	VIIA	—— VIIIA ——			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
H —																	He —
Li -47.5	Be -72.7											B -60.8	C —	N —	O —	F —	Ne —
Na -33.1	Mg -72.8											Al -80.2	Si -72.5	P -50.9	S -27.1	Cl —	Ar —
K -28.9	Ca -75.8	Sc -91.1	Ti -72.7	V -58.2	Cr -54.0	Mn -47.3	Fe -39.2	Co -30.9	Ni -28.8	Cu **-18.6**	Zn -41.9	Ga -51.7	Ge -46.2	As -31.2	Se -18.0	Br —	Kr —
Rb -26.3	Sr -70.7	Y **-91.1**	Zr -87.7	Nb -64.9	Mo -46.8	Tc -34.5	Ru -24.3	Rh -18.3	Pd -13.4	Ag -2.4	Cd -31.0	In -44.2	Sn -46.2	Sb -34.4	Te -25.8	I —	Xe —
Cs -27.0	Ba **-61.1**	La **-85.7**	Hf -88.7	Ta -69.8	W -50.3	Re -33.3	Os -23.5	Ir -19.3	Pt -5.6	Au > 0	Hg -10.9	Tl -18.6	Pb -26.2	Bi -27.3	Po ?	At —	Rn —
Fr ?	Ra -62.5	Ac ?															

Ce -87.1	Pr -87.2	Nd **-86.4**	Pm ?	Sm -87.6	Eu -82.5	Gd **-87.1**	Tb -87.3	Dy -89.1	Ho **-89.9**	Er -90.9	Tm -89.9	Yb **-86.7**	Lu -89.9
Th -97.7	Pa -97.5	U ?	Np ?	Pu ?	Am ?	Cm ?	Bk ?	Cf ?	Es ?	Fm ?	Md ?	No ?	Lr ?

— No relevant oxide
? No reliable data

FIG. 1

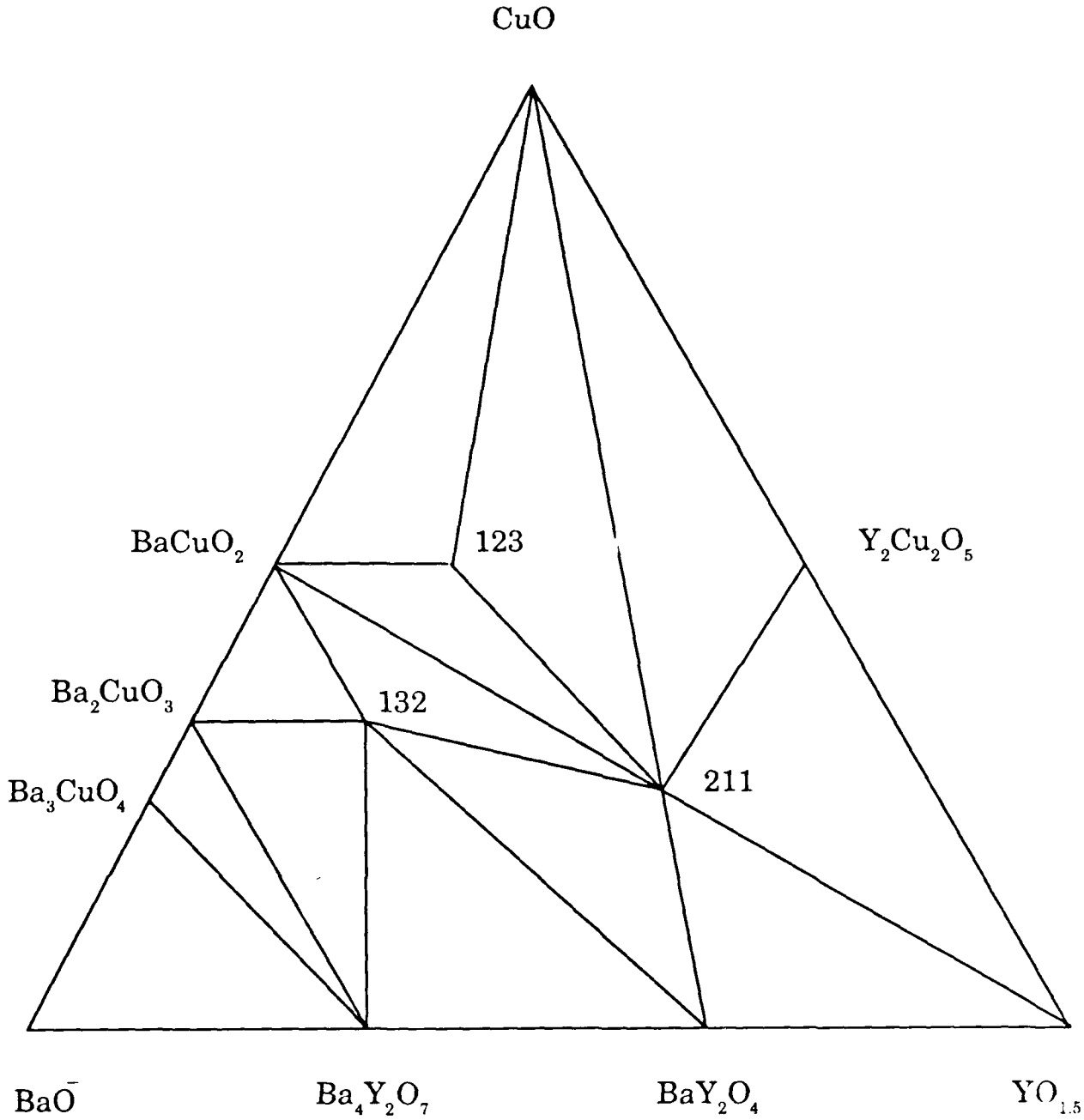
CuO
BaCuO2
123
Y2Cu2O5
Ba2CuO3
132
Ba3CuO4
211
BaO
Ba4Y2O7
BaY2O4
YO1.5

FIG. 2

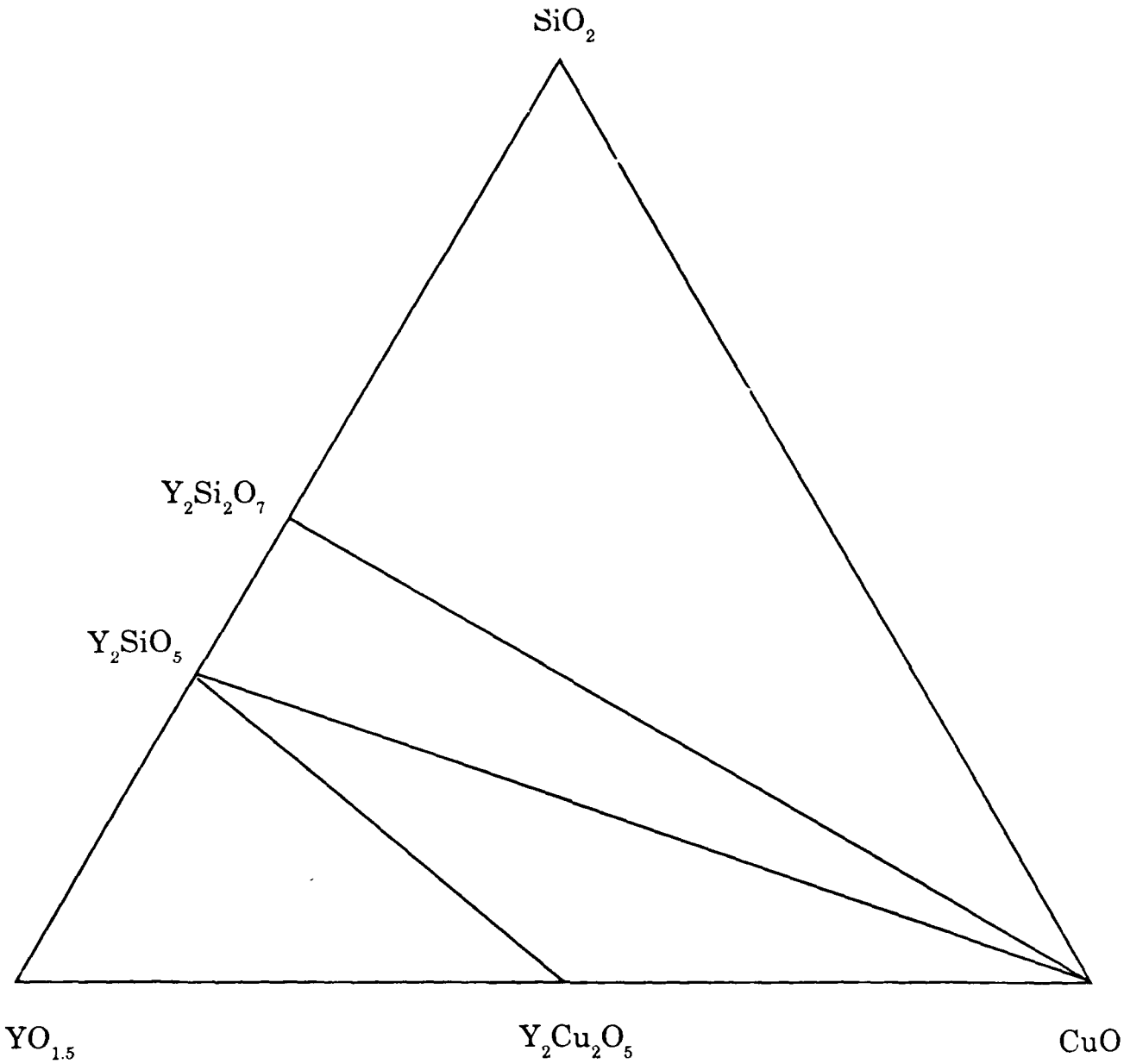

FIG. 3

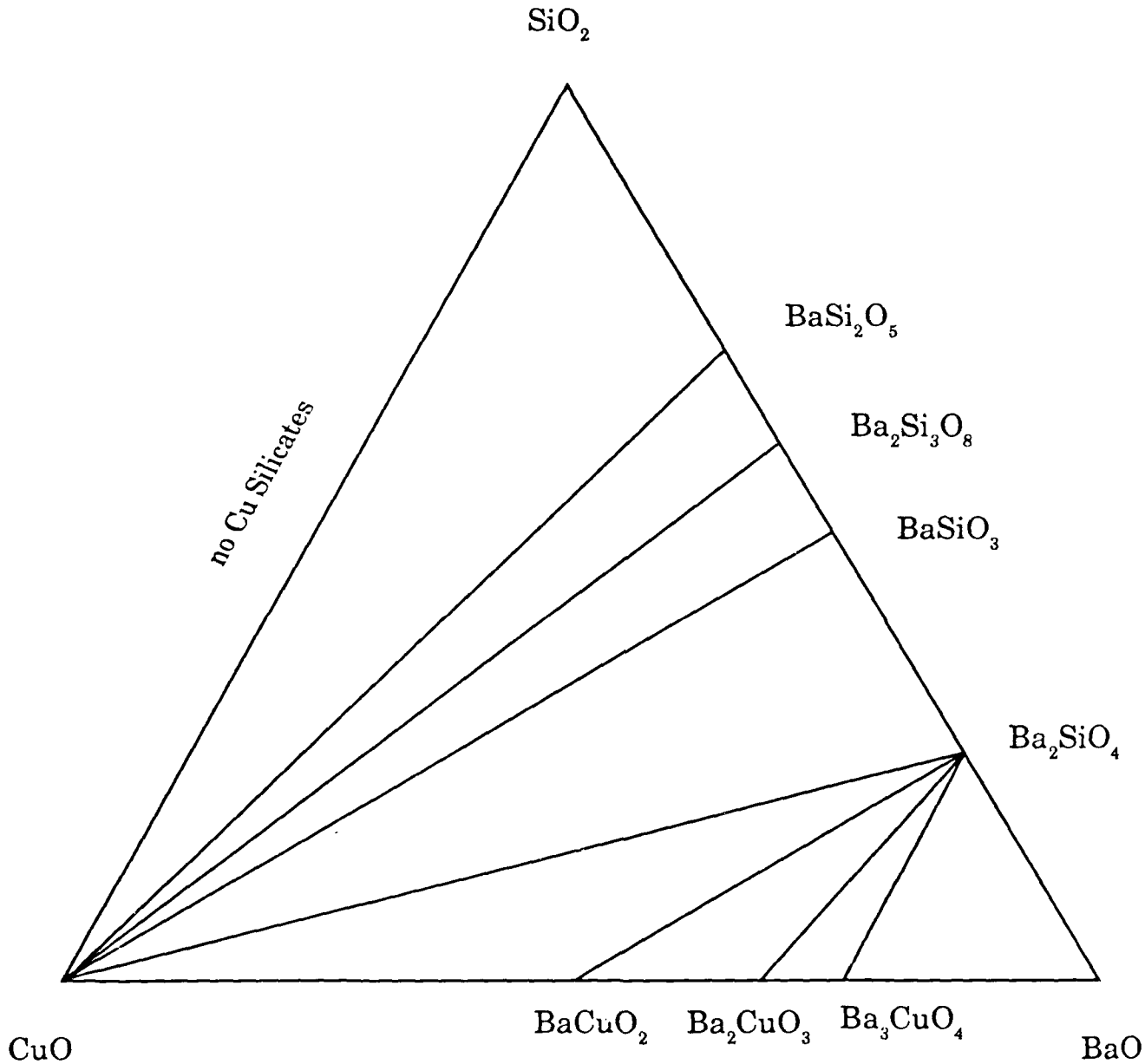
SiO_2
$BaSi_2O_5$
$Ba_2Si_3O_8$
$BaSiO_3$
Ba_2SiO_4
no Cu Silicates
CuO
$BaCuO_2$
Ba_2CuO_3
Ba_3CuO_4
BaO

FIG. 4

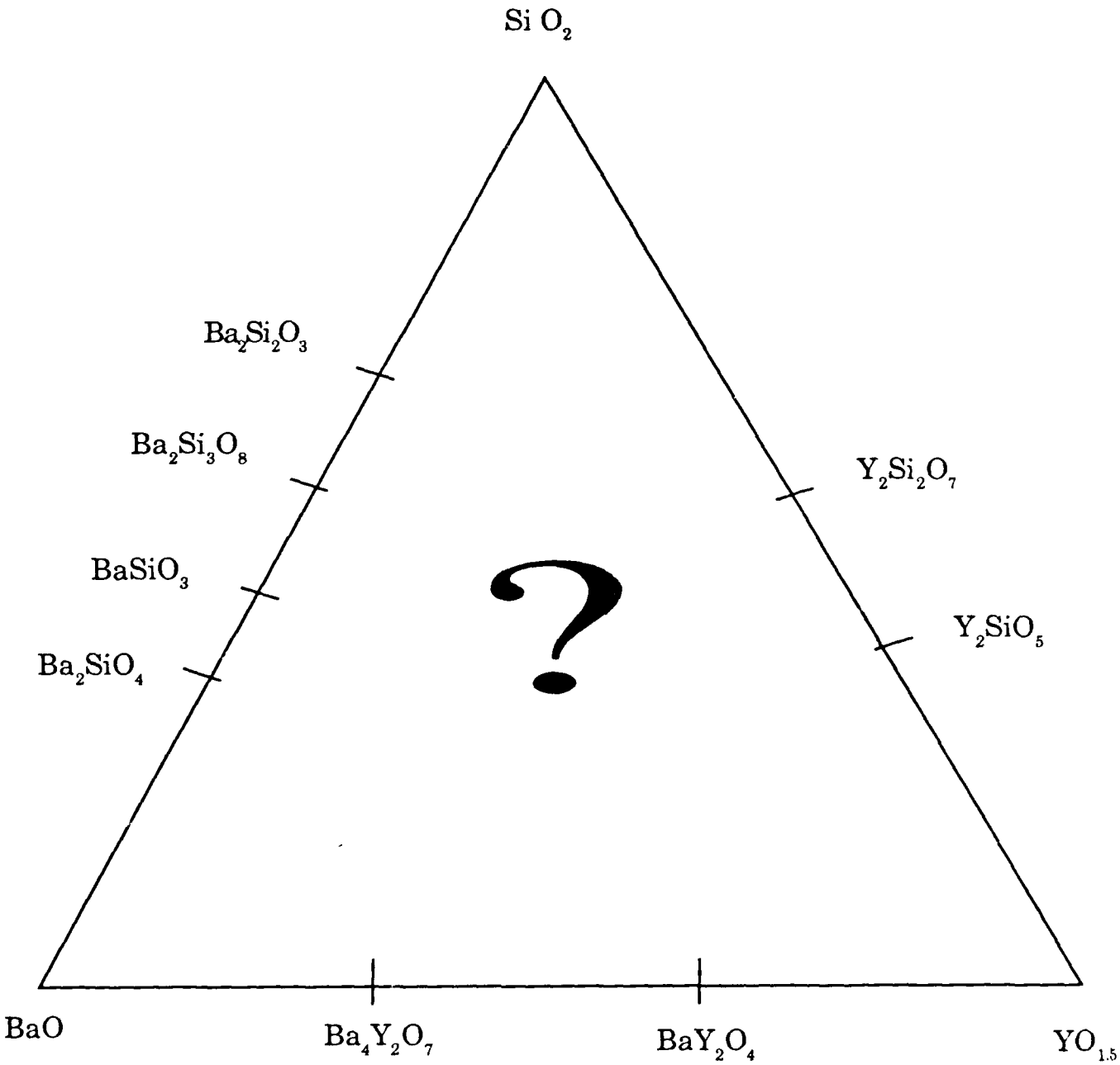
Si O_2
$Ba_2Si_2O_3$
$Ba_2Si_3O_8$
$BaSiO_3$
Ba_2SiO_4
$Y_2Si_2O_7$
Y_2SiO_5
?
BaO
$Ba_4Y_2O_7$
BaY_2O_4
$YO_{1.5}$

FIG. 5